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THE MATERIALS RESEARCH LABORATORY

THE PENNSYLVANIA STATE UNIVERSITY

TECHNICAL SUMMARY REPORT

TO

ADVANCED RESEARCH PROJECTS AGENCY

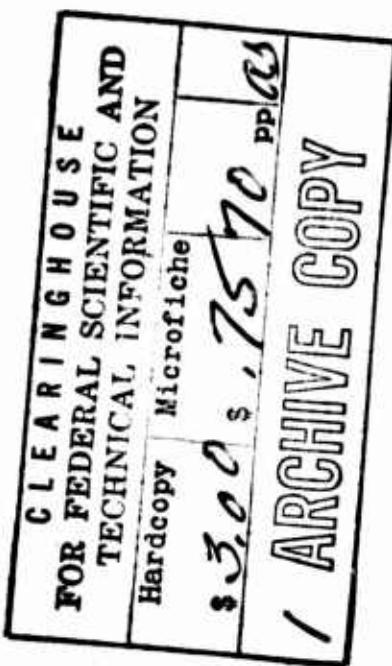
ON

MATERIALS PREPARATION AND CHARACTERIZATION RESEARCH

For the period 16 October 1965 to 30 June 1966

Contract No. DA-49-083 OSA-3140

ARPA Order No. 338, Amendment 2



UNIVERSITY PARK, PENNSYLVANIA

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~~RESEARCH PROGRESS AND RESULTS IN THE  
FOLLOWING ACTS ARE REPORTED~~

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## 1. INTRODUCTION: NATURE OF REPORT

This report officially covers the period from January 1, 1966 to June 30, 1966, for the new ARPA Contract DA-49-083 OSA-3140 supporting research on Materials Preparation and Characterization. In fact, this report includes work over a somewhat longer period due to delays in the contract negotiation.

Although the ARPA contract at Penn State does not constitute IDMRL funding it forms a cornerstone of the funding for the Materials Research Laboratory at The Pennsylvania State University. At the suggestion of ARPA we are including in this report a very brief account of the overall research in the MRL. The account will also demonstrate the relation between the ARPA support in the area of the preparation and characterization of materials to the varied research on the physical properties of these materials, which is supported from other sources, but which interacts closely with ARPA activities. Direct ARPA support is marked by means of an asterisk (\*) on the sub-headings of Sections 2, 4 and 5.

## 2. SUMMARY OF OVERALL RESEARCH EFFORT IN THE M.R.L.

In this section we list the faculty members and the students active in the Materials Research Laboratory program and follow it with a list of papers presented at meetings during the past year and the papers which appeared in print during the fiscal year July 1, 1965 - June 30, 1966.

## **2.1 Faculty involved**

H. A. Atwater - Associate Professor of Physics

G. R. Barsch - Associate Professor of Solid State Science

G. W. Brindley - Professor of Solid State Technology

W. R. Buessem - Professor of Ceramic Science

L. E. Cross - Associate Professor of Solid State Science

F. Dachille - Associate Professor of Geochemistry

H. K. Henisch - Professor of Applied Physics

M. C. Inman - Associate Professor of Engineering Mechanics

G. G. Johnson - Assistant Professor of Solid State Technology

B. E. Knox - Assistant Professor of Solid State Technology

H. A. McKinstry - Assistant Professor of Solid State Technology

A. Muan - Professor of Metallurgy

L. N. Mulay - Associate Professor of Solid State Science

D. M. Roy - Senior Research Associate in Geochemistry

R. Roy - Professor of Geochemistry and Director, Materials Research  
Laboratory

V. Vand - Professor of Crystallography

F. Vastola - Associate Professor of Fuel Science

K. Vedam - Associate Professor of Solid State Science

P. Walker, Jr. - Professor of Fuel Science

J. N. Weber - Assistant Professor of Geochemistry

E. W. White - Assistant Professor of Solid State Science

W. B. White - Assistant Professor of Geochemistry

## 2.2 Graduate students support:

Some 65 graduate students have been supported in their studies for advanced degrees - the vast majority for Ph.D. degrees. The largest number of the students are majoring in Solid State Technology (= Materials Science) with Physics, Engineering Mechanics, Electrical Engineering and Chemistry also represented.

## 2.3 Degrees granted

During the past year (July 1, 1965 - June 30, 1966) the following students received advanced degrees; the subjects of their dissertation is also included:

### Ph.D.

1. Ronald E. Barks. "Flux-Growth of Single Crystal  $R_2O_3$  Oxides with the Corundum Structure".
2. Dae-Hyun Chung. "Elastic Anisotropy of Single Crystals and the Polycrystalline Isotropic Elastic Moduli of Solids".
3. Peter J. Ficalora. "Oxidation Kinetics of Iron-Magnesium Oxide Mixed Single Crystals".
4. Gerald G. Johnson, Jr. "A Mathematical Analysis of Terrestrial Impact Craters".
5. Gerald Katz. "Topotactic Reactions in Precipitation from and Formation of Gallium Spinels".
6. Lloyd K. Keys. "Magnetic Susceptibility and Resonance Studies on Adsorbed Oxygen: Formation of  $O_4$  Species".
7. F. F. Lange. "Intrinsic Brittle Strength of Magnesium Oxide Bicrystals".

8. Vernon R. Porter. "Studies in the Titanium-Oxygen System and the Defect Nature of Rutile".
9. Otis D. Slagle. "The Elastic Constants of Some Alkali Halides as a Function of Temperature and Composition".
- \* 10. Eugene W. White. "Chemical Characterization of Materials by X-ray Spectroscopy".

M.S.

1. B. N. N. Achar. "Kinetic Study of the Dehydroxylation of Serpentine".
2. Fred I. Grace. "The Effects of Shock Waves on the Strength and Crystal Structure of 70/30 Copper-Zinc Alloy".
3. Robert O. Miller. "Phase Equilibrium Studies of Cadmium Sulfide by Static and Dynamic Methods".
- \* 4. James W. McCauley. "Control of Nucleation, Crystal Growth, and Doping of Various Calcium Carbonate Phases by the Gel Technique".
- \* 5. Lawrence B. Robinson. "The Epitaxial Growth of Several Transition Metal Monoxide and Ferrite Single Crystals".

2.4 Papers presented at meetings

The following papers were presented during the year by the faculty and students of the laboratory. The subject matter of these papers is a more up-to-date indication of current activity than the subsequent list of papers appearing in print since the latter are frequently 1-2 years behind.

- \* Balascio, Joseph F., William B. White and Rustum Roy. Growth of Single Crystal Selenium from High Pressure Liquid Ammonia. Am. Ceram. Soc., Washington, D. C. (Bull. Am. Ceram. Soc. 45, 371 (1966)).
- \* Barks, Ronald E. and Della M. Roy. Growth of Crystals of Chromium Sesquioxide ( $\text{Cr}_2\text{O}_3$ ) by the Flux Method. Am. Ceram. Soc. Mtg., Washington, May 1966.

Barry, Thomas L. and Rustum Roy. Defect Characterization and Precipitation from CaO-Y<sub>2</sub>O<sub>3</sub> Crystalline Solutions. Am. Ceram. Soc. Mtg., Washington, May 1966.

Barsch, G. R. Elastic Instability and Theoretical Strength for Brittle Fracture. AIME Mtg., Detroit, Oct. 1965. J. Metals (Abstracts) 17.9, 1029 (1965).

\* Berkes, John S. and William B. White. Determination of Structural Features of Alkali Borate Glasses Using the Optical Spectrum of Ni<sup>++</sup> as an Environmental Probe. Am. Ceram. Soc. Mtg., Washington, D. C. (Bull. Am. Ceram. Soc. 45, 420 (1966)).

Braunlich, P. Thermally Stimulated Recombination Processes in Photoconducting Crystals. Seminar of the Solid State Research Lab. in Harshaw Chemical Co., Cleveland, O., Dec. 1965.

Braunlich, P., D. Schaefer, A. Scharmann. Discussion of the Electron Balance Equation for Inorganic Photoconducting Crystals; and Experiments Pertaining to Infrared-Stimulated Luminescence. Int. Conf. on Luminescence Dosimetry, Stanford University, Palo Alto, Calif., June 21-23, 1965.

Brindley, G. W. Some Topics Concerning Organo-Silicate Complexes . Chevron Company, La Habra, Calif., Aug. 1965.

Brindley, G. W. Reaction Processes in Some Oxide Materials . Joint Meeting of Physics, Chemistry & Geology, University of Lisbon, Portugal, July 1965.

Brindley, G. W. Classification Scheme for the Phyllosilicates, Including the Layer Lattice Clay Minerals . Clay Min. Soc. Mtg., Berkeley, Calif, Aug. 1965.

Brindley, G. W. and Sally Wentworth. "Illite". Clay Min. Soc. Mtg., Berkeley, Calif. Aug. 1965.

Brindley, G. W. and Persio de Souza Santos. "New Varieties of Kaolin-Group Minerals and the Problem of Finding a Suitable Nomenclature".

Int. Clay Conf., Jerusalem, Israel, June 20-24, 1966.

Brindley, G. W., B. N. N. Achar, and J. H. Sharp. "Kinetics and Mechanism of Dehydroxylation Processes, III. Applications and Limitations of Dynamic Methods". Int. Clay Conf. Jerusalem, Israel, June 20-24, 1966.

Chang, Z. P., G. R. Barsch. D. L. Miller. Pressure Dependence of the Elastic Constants and Elastic Instability of Cesium Halides.

AIME Mtg., Detroit, Oct. 1965. J. Metals (Abstracts) 17.9, 1029 (1965).

Cross, L. E. Ferroelectricity: Some Current Problems in Single Crystals and Ceramics. Purdue University, Materials Research Seminar.

Cross, L. E., R. Kunz. Dielectric Properties of Calcium Fluoride Crystals and Ceramics 'Doped' with Trivalent Ions. Bull. Am. Ceram. Soc. 45, 379 (1966).

Cross, L. E., D. Chakravorty. Dielectric and Electro-optic Studies of the Polarization Process in  $\text{SrTiO}_3$  at Low Temperature. Internat'l. Mtg. on Ferroelectricity, Prague, Czechoslovakia, June 1966.

Dachille, Frank. Phase Equilibrium Studies of Cadmium Sulfide by Static and Dynamic Methods. Basic Science Div., Am. Ceram. Soc. Mtg., Pittsburgh, Pa., Sept. 1965.

Dachille, F. Experimental High Pressure Deformation of Crystals as a Guide in the Study of Putative Impact Structures, 28th Mtg. of the Meteoritical Soc., Odessa, Texas, Oct. 21-22, 1965.

Dachille, F. Shock Damage of Minerals in Shattercones. Geol. Soc. Ann. Mtg., Kansas City, Mo., Nov. 4-6, 1965.

Dachille, Frank and Rustum Roy. Difficulties in the Evaluation of

Solid State Phenomena and Reactions at High Pressures. Chem. Soc.  
Mtg., Pittsburgh, Pa., March 1966.

Dachille, F., and Rustum Roy. The Equilibrium Diagram for the Systems  
CdS and Ge, and Comments on the Kinetics of Phase Transitions.  
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Infrared Spectra of the Ordered Spinel-Like Phases  $\text{LiAl}_5\text{O}_8$ ,  
 $\text{LiGa}_5\text{O}_8$ , and  $\text{LiFe}_5\text{O}_8$ . Am. Ceram. Soc. Mtg., Washington, D. C.  
(Bull. Am. Ceram. Soc. 45, 383 (1966)).

Gibbs, G. V. and E. W. White. Structural and Chemical Effects on the  
 $\text{AlK}_\beta$  Emission Bands Studied with the Electron Probe. Presented  
at the First National Conference on Electron Probe Microanalysis,  
May 1966.

\* Hamaker, Raymond W. and William B. White. Growth of Crystalline  
Solutions by Temperature Gradient Zone Melting. Am. Ceram. Soc.  
Mtg., Washington, D. C. (Bull. Am. Ceram. Soc. 45, 371 (1966)).

\* Hanoka, J. I., K. Vedam, H. K. Henisch. Polytypism in Gel-Grown Lead  
Iodide. Presented at Internat'l. Conf. on Crystal Growth, Boston,  
June 20-24, 1966.

\* Harvill, M. L. and Rustum Roy. Hydrothermal Crystal Growth of  $\text{RO}_2$   
Oxides and Confirmation of the Hartman Theory for the Habit of  
Rutile Structure Crystals. ICCG Mtg., Boston, Mass., June 1966.

\* Harvill, M. L. and Rustum Roy. Mechanism of Solution of  $\text{GeO}_2$  and  $\text{SiO}_2$   
in "Hydrothermal" Environments. Am. Ceram. Soc. Ann. Mtg.,  
Washington, May 1966.

Johnson, G. G., Jr. Computer Preparation of Hanawalt-Davey Indices.

ASTM Meeting, June 1966.

Johnson, G. G., Jr. Computer Preparation of Fink Index, ASTM Ann.

Mtg., June 1966.

Jones, T. S., Shigeyuki Kimura and Arnulf Muan. Phase Relations in the System  $\text{FeO}-\text{Fe}_2\text{O}_3-\text{ZrO}_2-\text{SiO}_2$ . Am. Ceram. Soc. Mtg., Washington, May 1966.

\* McCauley, James W. and Rustum Roy. Evidence for Epitaxial Control of  $\text{CaCO}_3$ -Phase Formation as Mechanism of the Influence of Impurity Ions. 47th Ann. Mtg. AGU, April 19-22, 1966.

\* McCauley, James and Rustum Roy. Gel-Growth of Pure and Doped  $\text{CaCO}_3$  (Calcite) and  $\text{SrSO}_4$  Single Crystals. Am. Ceram. Soc. Mtg., Washington, May 1966.

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Muan, Arnulf. Phase Equilibria in Oxide Systems. Gordon Research Conf. on Chemistry of Molten Salts, Meriden, N. H., Aug. 1965.

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Cinnabar in Synthetic Ore Solutions: Trans. Am. Geophys. Union,  
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- Roy, D. M. and S. P. Faile. Microheterogeneity in Gas-Glass Systems.  
Am. Ceram. Soc. Mtg., Washington, May 1966. Bull. Am. Ceram.  
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- Roy, D. M. Element Segregation During Cement Hydration. Highway  
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- Roy, Rustum. The Relation of Phase Transition Theory and Kinetics  
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Conf. on High Pressures, Paris, France, Aug. 1965.
- \* Roy, Rustum. Application of the Isothermal Flux Evaporation Method.  
Int. Crystal Growth Meeting, Boston, Mass., June 1966.
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anisms of Inorganic Solids, Aberdeen, Scotland, July 1966.
- Roy, Rustum. Equilibrium and Kinetics in High Pressure Transitions  
from Diamond Structure Phases. Gordon Conf. on High Pressures,  
June 1966.
- Roy, Rustum. Crystal Chemical Effects of High Pressures. Am. Ceram.  
Soc. Mtg., Washington, May 1966.
- Schmidt, E. D. D., and K. Vedam. Variation of the Refractive Indices  
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White, William B. Sulfate Mineralogy in Some Caves in the United States. 4th Int. Congress of Speleology, Ljubljana, Yugoslavia, Sept. 1965.

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\* Berkes, John S., William B. White, Rustum Roy. Growth of Rutile of Controlled Composition from Borate Fluxes. J. Appl. Phys. 36: 3276-3280 (1965).

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## 2.6 Agencies supporting research

### Department of the Air Force:

Wright-Patterson Air Force Base, Systems Engineering Group

Contract No.: AF33(615)3360

### Air Force Office of Scientific Research:

Solid State Sciences Division

Grant No.: AF-AFOSR-208-63

### Department of the Army:

Defense Supply Service - Washington, Advanced Research Projects Agency

Contract No.: DA-49-083 OSA-3140

U. S. Army Electronics Command

Contract No.: DA-28-043 AMC-01304(E)

U. S. Army Engineer Research and Development Laboratories

Contract No.: DA-44-009-AMC-581(T)

U. S. Army Materials Research Agency

Contract No.: DA-19-066-AMC-325(X)

### U. S. Atomic Energy Commission:

Division of Biology and Medicine

Contract No.: AT(30-1)-3409

Metallurgy and Materials Program

Contract Nos. AT(30-1)-2887 and AT(30-1)-2581

### National Aeronautics and Space Administration:

Sub-grants under NASA Institutional Grant

Grant No.: NGR-39-009-015

Goddard Space Flight Center, Thermal Systems Branch, Spacecraft Tech.

Div.

Grant No.: NGR-39-009-042

National Science Foundation:

Engineering Materials, Engineering Division

Grant Nos.: GP-3232, GP-2033, GP-2291

Geochemistry, Earth Science Division

Grant Nos.: GP-4450, G-19231, GP-5102

Mathematical and Physical Sciences, Earth Science Division

Grant Nos.: GP-4502 and GP-5489

Office of Naval Research:

Metallurgy Branch

Contract Nos.: Nonr-656(20) and Nonr-656(27)

Public Health Service

National Institute of General Medical Sciences

Grant No.: GM09487-05

National Institute of Arthritis and Metabolic Diseases

Grant No.: GM-CA13891-01

3. SUMMARY OF ARPA CONTRACT RESEARCH

3.1 Research Achievements:

The separate reports below give details on the status of the research in various aspects of the program in preparation and characterization. It will be seen that several of the programs are now mature and are producing results steadily. We do not need - as in the past - to report any further on the establishment of the general facilities. These have now reached a more or less steady state level and, in the future, reference will only be made to major changes.

On the preparation side we have had considerable success with the vapor-pyrolysis epitaxial growth of 3-d element simples and complex oxides (such as NiO, MgFe<sub>2</sub>O<sub>4</sub>, etc.) as well as with the hydrothermal growth of GeO<sub>2</sub> and SnO<sub>2</sub>. The former offers considerable promise as a general method. An attempt will be made to determine its applicability

to various other materials.

On the characterization side the laser-ultramicroscope reported earlier is clearly a useful routine characterization tool. It is gratifying to report that the Air Force Cambridge Research Laboratories has funded contracts for the construction of an engineered version of the instrument developed here. We continue our specialization in the use of X-ray emission shifts to characterize the valence and structural environment of the lighter elements. The new ASTM standard X-ray emission wavelength tables have been published using the data provided from this project. A most interesting new tool developed in our laboratories is the laser microprobe time-of-flight mass spectrometer, with which it has been possible to obtain both the elemental composition and some structural information from a variety of solids. Most of this particular work is not supported by the ARPA contract but certain applications, for instance to the chemical composition of semiconductor junctions and surfaces, is attracting considerable attention.

### 3.2 Training

#### 3.2.1 Graduate students

We believe that one of the major contributions of this contract is to provide for the training of a substantial number of Ph.D. students in the field of materials preparation and characterization. We know of very few degree programs at U. S. Universities where the scientific course background and research experience appropriate for an advanced degree in this obviously critical field are available. The involvement of 15 students in this area, therefore, is significant.

Moreover, as the program is now in its fourth year, as may be expected, some of the students are now completing their degrees. Thus during the last year: 3 students completed Ph.D.'s, two in the

area of crystal growth and another in materials characterization, while 2 others finished M.S. degrees in the crystal growth area. Their names and subjects are included in the overall list given in the last section.

### 3.2.2 Short courses; coupling with industry

We continued to provide our annual two-week short course in materials preparation and characterization for research personnel in industry, government and universities.

Our Industrial Coupling Program likewise continues to operate with very promising results. It involves close research cooperation between a (self-) selected small group of companies and the Materials Research Laboratory. We believe that this has been very rewarding in many ways. One of these is the keen awareness of problems which are of interest to industry and government which has been transmitted to the students and faculty. In several instances it has engendered joint work in new fields.

#### 4. RESEARCH RESULTS: MATERIALS PREPARATION

##### 4.1 Growth of "Large" Crystals

###### 4.1.1 Flux Method

###### 4.1.1.1 Oxide crystals having the corundum structure \* (R. E. Barks and D. M. Roy)

$\text{Fe}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$ , have been grown from sodium, potassium and lead borate solutions. The relationship between various crystal growth parameters important in the flux method and their effect on the resulting crystals has been determined with respect to crystal properties. These include chemical analysis, etching techniques for dislocation studies, surface feature examination and weight fraction analysis to obtain the crystal size distribution. These properties have been related to the growth parameters in order to provide a concept of the growth process, and in order to evaluate those factors to be considered in selecting the optimum combination of growth parameters and flux.

Ruby crystals grown in this study were used in an investigation of the red-green color change in the system  $\text{Al}_2\text{O}_3$  -  $\text{Cr}_2\text{O}_3$ . The mechanism of this change has been related to the subsolidus phase equilibria of the system.

The stability fields of the desired  $\text{R}_2\text{O}_3$  phases in their respective growth systems have been determined. Weight loss with time studies were conducted in order to ascertain the evaporation behavior of the molten solutions. This combined information aids in the selection of a growth technique. Growth by flux evaporation is favored in systems exhibiting low solubility of the primary phase and a steeply sloping liquidus curve, indicative of a high partial molar heat of solution. Growth by flux evaporation or slow cooling can be utilized in systems with more gently sloping liquidus curves indicative of greater solubility per unit temperature and low heat of fusion. The choice of technique depends on the nature of the specific system.

Despite the wide variety of growth conditions employed, the chemical impurity contents and etch pit densities of crystals grown by a specific technique for a given system remained relatively constant. Crystals grown by slow cooling generally exhibited the lower values for each of these properties.

The principal effect of the various growth parameters was observed in the habit and size distributions of the crystals. This reflects the operation of various growth mechanisms in response to the conditions imposed.  $0001\bar{}$  is the major face under the widest variety of conditions.  $10\bar{1}2$  becomes the dominant face above a certain temperature. This temperature increases with decreasing solubility in solution or with increasing viscosity. The optimum growth conditions for a given compound correlate with a mono-modal crystal size distribution indicating the dominance of a single growth mechanism during the entire growth process.

The flux-primary phase combinations employed in this study satisfy the requirements of Dietzel's field strength hypothesis. The borate fluxes employed are crystallo-chemically favorable for the growth of corundum structure oxides permitting high solubility while being chemically incorporated in the crystals to a negligible extent. The problem of flux dissociation at high temperatures can be overcome by a knowledge of both the system and the interplay of the various growth parameters.

The color change in the system  $\text{Al}_2\text{O}_3 - \text{Cr}_2\text{O}_3$  was investigated by observing the effect of increasing concentration of  $\text{Cr}_2\text{O}_3$  and temperature on the lattice constants and absorption spectra of the crystalline solutions. This is interpreted with reference to the phase equilibrium of the system. The change corresponds to a continuous shift in the absorption maxima with increasing temperature. As a function of composition, the mechanism depends

on the temperature at which the solvus curve intersects the color change region. Above this, the change correlates with continuous alterations in the absorption spectra and lattice constants. The color change below this temperature occurs due to the exsolution of a second,  $\text{Cr}_2\text{O}_3$  -rich green phase.

Exploratory work with growth of  $\text{AlFeO}_3$  and  $\text{GaFeO}_3$  has been conducted. Fe-doped  $\text{Al}_2\text{O}_3$  crystals have been prepared for optical studies.

The Ph.D. dissertation of Mr. Ronald E. Barks, "Flux Growth of Single Crystal  $\text{R}_2\text{O}_3$  Oxides with the Corundum Structure" was completed during this period. Three papers describing this work have been presented at various meetings .

#### 4.1.1.2 Nucleation Studies in Simple Flux Systems \* (J. S. Berkes, W. B. White and R. Roy)

This investigation was initiated in order to study, in detail, the nucleation and subsequent growth of a transition metal oxide from a network forming solvent. The transition metal oxide is NiO and the solvents under current investigation are  $\text{Li}_2\text{B}_4\text{O}_7$ ,  $\text{Na}_2\text{B}_4\text{O}_7$ ,  $\text{K}_2\text{B}_4\text{O}_7$  and  $\text{Rb}_2\text{B}_4\text{O}_7$ .

The parts of the investigation completed to date are:

1) Phase equilibria in the binary systems

- a) NiO -  $\text{Li}_2\text{B}_4\text{O}_7$ , partially completed
- b) NiO -  $\text{Na}_2\text{B}_4\text{O}_7$ , completed
- c) NiO -  $\text{K}_2\text{B}_4\text{O}_7$ , completed to be published soon
- d) NiO -  $\text{Rb}_2\text{B}_4\text{O}_7$ , completed

2) Site symmetry studies of the  $\text{Ni}^{++}$  ion, in the above mentioned alkali borate liquids, have been completed. An abstract of an oral paper describing this work is quoted below:

Determination of Structural Features of Alkali Borate Glasses Using the Optical Spectrum of  $\text{Ni}^{++}$  as an Environmental Probe

"Optical absorption spectra have been obtained over the range of 0.3 to 3.0 microns on a series of alkali borate glasses containing nickel oxide.

The characteristic spectrum of  $\text{Ni}^{++}$  allows some conclusions to be drawn about the environment of the ion, which in turn allows some deductions to be made about the glass structure.

The  $\text{NiO}$  concentration was 10 mole percent in a glass composition range of 100%  $\text{K}_2\text{B}_4\text{O}_7$  to 100%  $\text{Na}_2\text{B}_4\text{O}_7$ . The spectrum of the high soda composition is characteristic of 6-coordinated  $\text{Ni}^{++}$ . When the potash concentration exceeds 50%, a portion of the nickel ions shift to 4-coordinated sites. There is a pronounced change in the site distribution with temperature. An interpretation of these efforts is made in terms of the breakup of the borate network by the potassium ions."

During this part of the investigation, which was carried out by spectroscopic methods, computer solutions of the Tanabe-Sugano secular equations were obtained for  $d^8$  and  $d^2$  electronic configurations to aid in the interpretation of the spectroscopic data.

Subsequently, solutions of the Tanabe-Sugano secular equations have been obtained for  $d^n$  ( $n = 3, 4, 5, 6, 7$ ) electronic configurations.

Parts of the investigation to be completed are:

- 1). Phase equilibria of the system  $\text{NiO-B}_2\text{O}_3$ , to help predict the ternary relationships in the alkali oxide -  $\text{B}_2\text{O}_3-\text{NiO}$  systems which will be necessary if crystal growth is carried out in open systems.
- 2). Nucleation kinetics of  $\text{NiO}$ , as a function of the different alkali borates which serve as solvents.
- 3). Crystal growth of  $\text{NiO}$  in these systems.

#### 4.1.2 Hydrothermal Growth

##### 4.1.2.1. Growth of Rutile-Structure Oxides \* (M. L. Harvill, R. Roy)

A major study on the mechanism rate of transport and actual growth of three isostructural oxide phases ( $\text{SnO}_2$ ,  $\text{TiO}_2$ ,  $\text{GeO}_2$ ) is now complete and has been reported in detail in the Ph.D. thesis of M. L. Harvill. These results have also been presented in three separate papers at various scientific meetings, and are currently being sent in for publication. A short abstract of the thesis is included below:

"Hydrothermal Crystal Growth of the Rutile Structure Oxides  $\text{TiO}_2$ ,  $\text{GeO}_2$ , and  $\text{SnO}_2$ "

Single crystals of three rutile-structure group IV oxides were grown hydrothermally up to 5mm in size. Growth conditions were 600-700°C, 4100 bars, and 80-100°C ΔT for  $\text{TiO}_2$  in 9M  $\text{H}_2\text{SO}_4$ ; 700°C, 4100 bars, and 100°C ΔT for  $\text{SnO}_2$  in 2M KOH; 450-700°C, 1000-4100 bars, and 50-100°C ΔT for  $\text{GeO}_2$  in  $\text{H}_2\text{O}$ .

All crystals were prepared to 99.99 per cent cation purity, and total OH content as measured by infra-red absorption for  $\text{TiO}_2$  was even less than in flame fusion material. Dislocation densities of  $\text{TiO}_2$  were less than crystals prepared by other means.

The potential of adding controlled amounts of impurities to  $\text{TiO}_2$  was demonstrated. Both Ni and Sn increased the dislocation content of  $\text{TiO}_2$ , but Ge had no detectable effect.

The solubility (S) of  $\text{GeO}_2$  in  $\text{H}_2\text{O}$  was found to be a function of the density ( $\rho$ ) of pure water at the experimental conditions according to the equation  $S = k_1\rho + k_2\rho^2 + k_4\rho^4$  (where k's are constants). This may indicate that a species  $\text{GeO}_2 \cdot n\text{H}_2\text{O}$  is formed, and  $n = 1$  dominates at low densities (pressures);  $n = 2$ , intermediate densities; and  $n = 4$ , at high densities. However, the model is not unambiguous.

The Hartman theory of crystal morphology was confirmed for rutile structure crystals. A modification was introduced in that if a screw dislocation is perpendicular to an F-face, S-faces may appear. The shape of crystals depended on the degree of super-saturation, but for super-saturations the dimension ratio  $2 <001>/(<100> + <010>)$  approached a value of 1.5.

#### 4.1.2.2. Sphalerite-Wurtzite Stability Relations\* (H. L. Barnes and S. D. Scott)

Sphalerite and wurtzite are generally regarded as polymorphs of stoichiometric ZnS with an inversion temperature near 1020°C. However, there are many apparent "anomalies" in the inversion temperature ranging from 850° to above 1175°C recorded in the literature. These and many other results suggest that at low total pressure the sphalerite-wurtzite inversion is not invariant. This has been investigated by two methods - hydrothermal experiments in sodium hydroxide solutions and solid + gas reactions at one atmosphere pressure and high temperature.

##### Hydrothermal Experiments

As reported previously, both cubic (sphalerite) and hexagonal (wurtzite) zinc sulfide crystals up to 5 mm. in diameter have been routinely grown in sodium hydroxide solutions by hydrothermal methods. Runs were made over a temperature range of 250-650°C using 10-50° gradients at pressures up to 9000 psi. A well-defined univariant curve at low total pressure separates the wurtzite field at higher temperature from the sphalerite field at lower temperature (Figure 1). The curve passes through 463° in 15 molal NaOH; 478° in 10.8 molal NaOH; 485° in 10 molal NaOH; and 516° in 6.2 molal NaOH, and has been reversed in each solution. As yet, wurtzite has not been found in runs using 4 molal NaOH up to 580°C nor in 2 molal NaOH as high as 650°C. These experiments have produced euhedral wurtzite crystals at as much as 550° below the so-called "inversion" temperature of 1020°C. This univariant

curve is a function of temperature and of fugacity of sulfur,  $f_{S_2}$ , controlled by the aqueous solution; oxygen fugacity is low and fixed near the sulfide-sulfate boundary.

#### Solid + Gas Experiments

Confirmation of the univariant relation noted in the hydrothermal experiments is found in anhydrous experiments with  $H_2$  and  $H_2S$  gases at one atmosphere pressure and high temperatures. Under hydrogen sulfide, wurtzite was converted to sphalerite between 500 and 900°C at  $f_{S_2}$  of  $10^{-2.5}$  to  $10^{-1.4}$ .

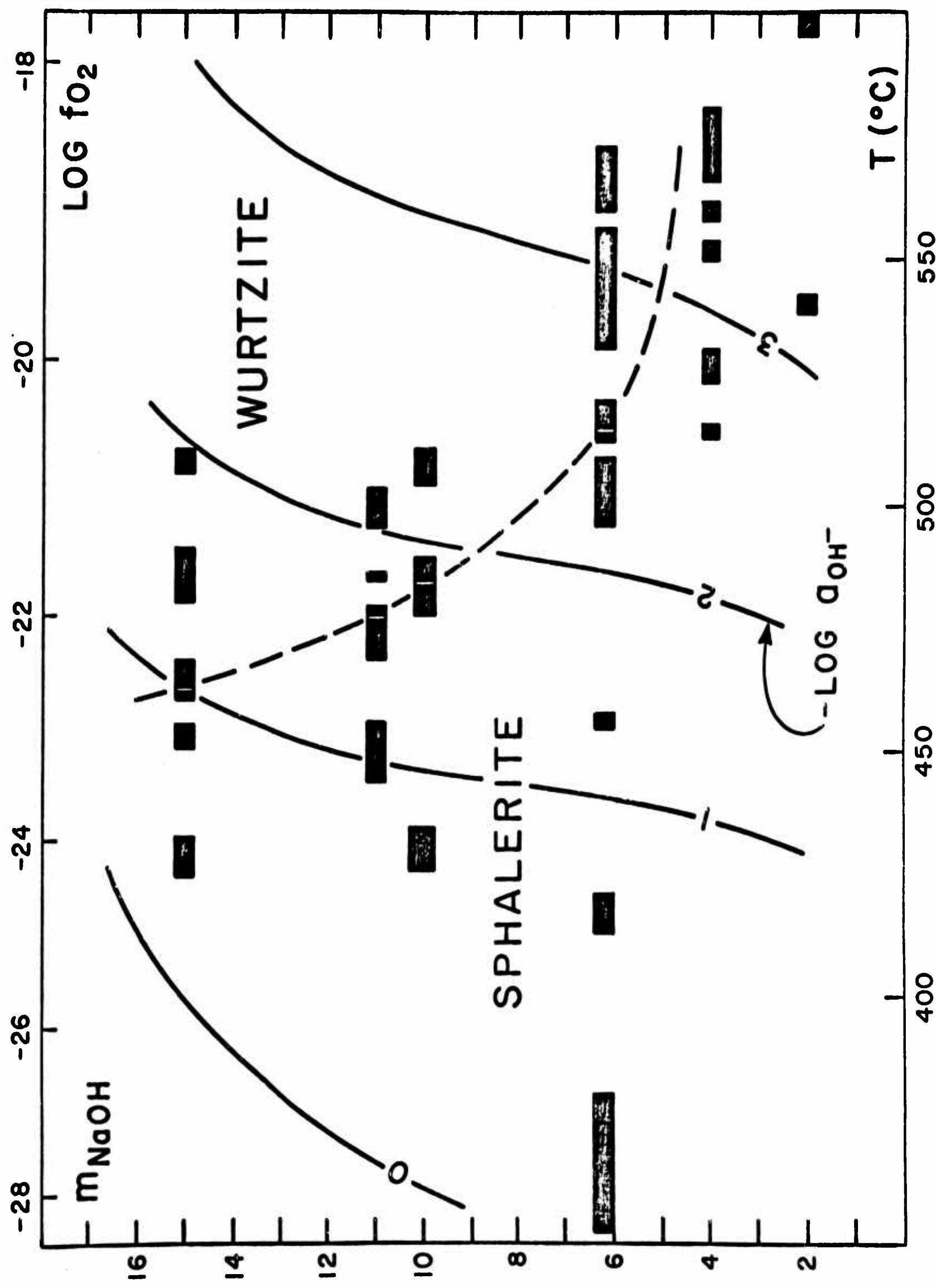
The explanation of these experiments is quite simple. Removal of sulfur from sphalerite by hydrogen produces a sulfur-deficient phase which is wurtzite. Addition of sulfur to wurtzite through the thermal dissociation of  $H_2S$  produces a sulfur-rich phase which is sphalerite.

On the basis of the hydrothermal and solid + gas experiments, the sphalerite-wurtzite phase change is not invariant but is a univariant function of  $f_{S_2}$  and temperature. Wurtzite occurs at low and sphalerite at high  $f_{S_2}$ . Unfortunately, there is not yet enough thermodynamic data available to calculate accurately the equilibrium  $f_{S_2}$  in the hydrothermal experiments. However, the gas experiments are being continued by mixing  $H_2$  and  $H_2S$  to allow determination of the sphalerite wurtzite phase boundary as a function of  $f_{S_2}$  over a wider temperature range.

Polytypism in the hydrothermally grown wurtzites is being investigated by single crystal x-ray techniques to determine their stability regions. To date, 6H and 4H polytypes have been synthesized. In addition, the unit cell sizes of sphalerite as a function of non-stoichiometry are being investigated. Preliminary results show that cell size decreases with lowering  $f_{S_2}$ .

The results of these investigations were presented at the Annual Meeting of the American Geophysical Union in Washington, April 1966.

Figure 1. Univariant phase boundary (dashed line) as a function of molality NaOH and temperature at 1/2 kilobar pressure. Boxes indicate runs conditions. Contours are calculated hydroxyl ion activities.



## 4.1.2.3.

Hydrothermal Growth of HgS Crystals\*  
(H. L. Barnes and S. D. Scott)

During a study of the solubility of HgS in NaOH-H<sub>2</sub>S hydrothermal solutions in this laboratory (Romberger et al, 1966), large cinnabar crystals up to 3 mm. diameter were grown in the cooler parts of the autoclave. From the data, it was evident that a cold-finger technique could be successful in growing mercury sulfide crystals in this system of well-known chemistry. The cold-finger consists of a stainless steel outer jacket and an inner tube through which a cooling medium, usually water, can be passed. The assembly is used with the rocking autoclave described by Barnes, 1963.<sup>+</sup> In a molal NaHS solution at 150°C, cold-finger temperature 27°C, pressure 300 psi, a 1 mm. thick druse of red HgS crystals (cinnabar) coated the cold-finger in a week. The crystals which displayed pinacoid and rhombohedral faces were small, owing to the large solubility gradient and rapid transport. Nucleation and rate studies are underway to produce larger crystals principally by reducing the solubility gradient and rate of transport.

4.1.2.3. Growth of Hexagonal Selenium in High Pressure Liquid Ammonia \*  
(J. F. Balascio, W. B. White and R. Roy)

Hexagonal crystalline selenium possesses a high degree of covalency as well as Van der Waals bonding between adjacent chains of selenium atoms. Liquid ammonia was employed as the solvent for the hydrothermal growth runs because it possesses a greater ability to dissolve covalent substances than water because it is less polar.

<sup>+</sup>Barnes, H. L. (1963) Ore solution chemistry. I. Experimental determination of mineral solubilities: Econ. Geol., v. 58, no. 7, p. 1054-1060.

One hundred and eleven runs were made, using selenium powder as the nutrient. Of these, 73 runs were made in gold capsules and 38 in teflon capsules.

### 1) Gold Capsule Results

Thirty-one runs produced hexagonal selenium. The parameters varied in these runs were pressure, temperature, capsule length, capsule type and run length. Pressure was varied from 7,700 psi to 28,600 psi; the temperature from 129°C to 737°C, capsule length from 3 to 2 inches, capsule types employed were double convection cells and monocells (capsules without a baffle) and the run length from 48 to 168 hours. The optimum growth conditions ascertained in gold capsules were a pressure interval of 14,000 - 15,200 psi with a temperature range of 175 to 192°C in a 2 inch double convection cell with a run length of 72 to 96 hours.

### 2) Teflon Capsule Results

Twenty-nine runs produced hexagonal selenium. All teflon runs employed double convection cells and run length was 72 hours. For the most part, the pressure was kept within the limits of 14,000 - 15,000 psi and the temperature was 190°C. The parameters varied in the teflon capsule runs were the capsule length, percent plug opening and percent baffle opening. From this experimentation, it was ascertained that the optimum conditions for growth in a teflon capsule 7 inches in length was a baffle opening of 1% and a plug opening range of 2 to 4%.

Weissenberg and oscillation photographs were taken of the crystals growth in the teflon capsule runs. The lattice parameters determined were  $a_0 = 4.34\text{\AA}$  and  $c_0 = 4.97\text{\AA}$ . From the Weissenberg photographs it was ascertained that the ammonia-grown selenium crystals possess a high degree of crystallinity and are indeed single crystals.

Semi-quantitative analyses showed that the crystals grown in the teflon capsules are of much higher purity than the ones grown in the gold capsules. The purity of the teflon capsule-grown crystals was estimated at 99.90%, that of the crystals grown in gold capsule was 98.70% and the purity of the starting materials are estimated at 99.96%.

The crystals obtained in the gold capsule runs reached a length of 5 mm with a width of approximately 0.1 mm; the crystals obtained in the teflon runs reached a length of 8 mm with approximately the same width as those grown in the gold capsules. The crystals obtained in both capsule runs possessed a needle-like morphology with the  $10\bar{1}0$  faces parallel to the growth direction. The growth direction was along the c-axis direction.

This study is complete and is being written up as the M.S. Thesis of J. F. Balascio.

#### 4.1.3. Growth from Melt

##### 4.1.3.1. High Temperature Kyropoulos Technique \* (K. Vedam and W. B. White)

The small crystal puller has been re-built to provide for better furnace temperature control and fume venting. It has been used for pulling alkali halides and in some experimentation to see if  $\text{BaTiO}_3$  can be pulled from flux solutions. A new and larger puller is under construction. It employs a 15 kw R. F. Generator and heavy duty pulling assembly. The installation of the generation, machining of the pulling device, and construction of the control assembly is complete. Remaining to be done is the construction of the temperature control circuits and the installation of the Iridium Crucible-Susceptor (now on order). With this device it should be possible to pull crystals of substances with melting points to  $2100^\circ\text{C}$ .

## 4.1.3.2.

Growth of Crystals By Arc-Fusion \*  
(L. Brown and W. B. White)

A small (3 x 3 foot) arc melting furnace has been constructed for the growth of MgO and related materials from the melt. In essence, the method consists of melting a pool of MgO in the center of an MgO polycrystalline mass using 15 - 25 kw power through carbon electrodes. The pool is allowed to cool and crystallize by gradually lowering the power. Initial experiments with hand controlled electrodes yielded MgO crystals up to one cm on an edge. Current work involves the construction of an automatic advance system for the electrodes in hopes of getting more uniform cooling. This construction is nearly complete.

4.1.4. Traveling Solvent Method

## 4.1.4.1.

Mechanism of Zone Migration \*  
(R. W. Hamaker and W.B. White)

Zone migration studies have been completed for the migration of both In and Pb zones through InSb in the temperature range between 400° and 450°C. The growth mechanism in both cases appears to be that due to a two-dimensional nucleation mechanism of layer formation. This has been confirmed from both interface velocity versus zone thickness data and from observations of final growth surfaces once the zone metals have been etched away. Both 110 and 111 "B" InSb seed orientations were used in this work. Maximum growth rates as large as  $1.2 \times 10^{-6}$  cm/sec (i.e., 0.04 mm/hr) were achieved. Single crystal regrowth regions as large as 3 mm were obtained.

## 4.1.4.2.

InSb-GaSb Solid Solutions\*  
(R. W. Hamaker and W. B. White)

The migration of both In and Pb zones through polycrystalline  $\text{Ga}_x\text{In}_{1-x}\text{Sb}$  has been accomplished, using InSb as a seed substrate. After about 2 mm of regrowth, uniform concentration were obtained. This was made evident through electron-probe scans of sectioned zones.

#### 4.1.5. Vapor Growth

##### 4.1.5.1.

##### Vapor Growth of Transition Metal Oxide by Halide Vapor Hydrolysis \* (L. B. Robinson, W. B. White and R. Roy)

This study is now complete and has been successfully defended as the M. S. Thesis of L. B. Robinson. A Summary of the thesis is given below.

The Cech method of epitaxial crystal growth has been conveniently used to study the growth of several transition monoxides and ferrites. Specifically, single crystals of NiO, CoO, FeO,  $\text{Co}_3\text{O}_4$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{NiFe}_2\text{O}_4$ , and  $\text{CoFe}_2\text{O}_4$  were grown epitaxially on MgO substrates by hydrolysis of the anhydrous metal bromide in the gaseous phase.

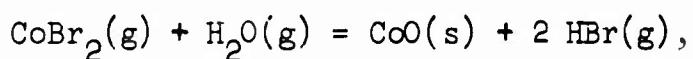
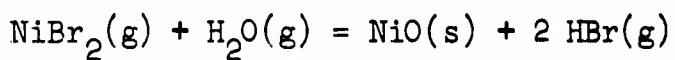
The development of the Cech vapor growth process into a reliable method for the preparation of oxide crystals required an investigation of several process parameters, an examination of the overgrown crystal by established analytic techniques, and a knowledge of the growth mechanism. The optimum growth conditions were found to depend primarily on: (1) the nature of the substance deposited, (2) the condition of the substrate, (3) the temperature of the substrate, (4) the halide sublimation temperature and vapor pressure and (5) the water vapor partial pressure.

In forming the monoxides only a water vapor atmosphere was used except in the preparation of wustite. Water vapor plus oxygen gas was used in the preparation of the ferrites and air for magnetite. All of the crystals were grown at temperatures below 700°C and at a total pressure of less than 25 mm Hg. The deposition was usually complete after approximately 30 minutes and the crystals were of uniform thickness with a glassy-clear smooth surface. By repeated deposition these crystals can be formed in various thicknesses suitable for a variety of studies. If desired, the overgrowth can be removed from

the substrate by using several acids for MgO dissolution. Thermodynamic calculations can be used to indicate the feasibility of the vapor hydrolysis of the halide at various temperatures. In addition, a knowledge of the thermodynamic aspects of the chemical reaction is helpful for understanding and controlling the deposition process.

The crystals were examined by X-ray diffraction, optical microscopy, electron microscopy, electron probe and etching techniques to determine their quality and for characterization. The crystals were found to deposit in parallel alignment with the (100) plane of MgO and  $10^3$ - $10^5$  dislocation/cm<sup>2</sup> were observed in NiO. In polycomponent compounds it appears that the deposit will assume certain equilibrium forms depending on the composition. Since this vapor process is one of sublimation or distillation, it is in itself a purifying process and a substantial increase in purity is observed.

In accordance with the chemical reaction equation, for example for the formation of NiO or CoO from the halides concerned:



one would expect at first a simple reaction mechanism. This did not appear to be the case when attempts were made to explain the conditions of growth, stability and morphology. Qualitative observations of the growth process indicated that nucleation and crystal growth proceeded from an intermediate liquid stage. A reaction mechanism is proposed which involves: (1) the formation of a hydroxybromide intermediate with fluid properties, (2) adsorption on the MgO substrate followed by (3) the chemical disproportionation-crystallization of the intermediate phase.

Probably the most important advantage of this method is the relatively low temperatures required in the crystal growth. The necessity of such a low temperature methods is very evident when one realizes that higher temperatures tend to dissociate the higher valence oxides and to require more complicated systems. The equipment requirements are very modest in comparison to the usual epitaxial systems. This method has the added advantage that deposition occurs only on the substrate and not throughout the reaction tube. The process also has an advantage over the chemical transport method for oxide growth in that the process is very rapid and does not involve the direct use of corrosive HBr or HCl atmospheres.

The main limitation in this work has been the lack of an identification of the intermediate species. The enhanced volatility of many compounds in the presence of steam is well known. However, little quantitative data are available, and the chemical composition of the volatile species is seriously in doubt in most cases. Therefore, for several reactions, assumptions had to be made on the formulae of both the sublimed species and the intermediate liquid phase.

#### 4.1.5.2. Vacuum deposited films of PbO-base mixtures\* (A. Auriol and R. Roy)

This study is concerned with the formation of short range order films by multi-source vacuum evaporation. PbO was selected as the "host" material and various other substances have been evaporated with it with the results shown below:

- (i) PbO-Pb mixtures: Pure lead films give polycrystalline layers with a strong preferred orientation on <111> plane. PbO films give the diffraction lines of both orthorhombic and tetragonal polymorphs. Mixtures give films which are always crystalline but with broadened diffraction peaks.

(ii) PbO-Zn mixtures: These films are polyphasic with PbO, Pb, ZnS and ZnO in varying proportion due to an exchange reaction in the gas phase.

(iii) PbO-GeO<sub>2</sub> mixtures: GeO<sub>2</sub> forms non-crystalline films when deposited alone. Mixtures up to 60% GeO<sub>2</sub> are nearly amorphous although their crystallinity increases with aging.

#### 4.2. New Techniques

##### 4.2.1. Crystal Growth in Gels

###### 4.2.1.1. Preparation of Gel-grown Crystals \* (H. K. Henisch and J. Dennis)

The studies on PbI(OH) described in the report of June 1965 has since been published: "Preparation and Properties of Lead Hydroxy-Iodide in Single Crystal Form," by J. Dennis, H. K. Henisch and P. Cherin, J. Electrochem. Soc. 112, 1240 (1965).

The work carried out since then has been mostly concerned with nucleation processes which are, of course, the key to the practical exploitation of the method. A paper on this subject is now in an advanced state of preparation. Heterogeneous nucleation can be easily demonstrated, as one would expect. It involves epitaxial growth on a substrate and shows, inter alia, that the gel method can be used for the preparation of heterojunctions. Foreign nuclei are always present in abundance, but most of them are rendered ineffective by being embedded in the gel. It is believed that the success of the gel growth method is crucially dependent on this process. With foreign nuclei wholly or, at any rate, sufficiently immobilized, it is possible to demonstrate homogeneous nucleation and to exercise a good deal of control over it. This can be done in various ways:

- (a) by programming the concentration of the diffusants,
- (b) by altering the pore size of the gels (e.g. by using sodium-aluminum gels of varying composition).

- (c) by changing the molecular size of the diffusing components, and
- (d) by means of trace impurities.

By exercising this kind of control, the number of crystals which grow competitively in any one growth system can be substantially reduced, with a corresponding increase in size and perfection. For example: photoconducting (and cathodoluminescent)  $\text{PbI}_2$  crystals have been grown as near-perfect hexagonal plates, up to 18 mm in diameter. The above methods of control are not limited to  $\text{PbI}_2$ , but how generally they can be applied remains to be seen.

Because the formation of a critical nucleus is expected to depend on the interface energy of the nucleus, it is expected to be sensitive to trace impurities, in the same way in which etching has been shown to be sensitive. Experiments are in progress to clarify these relationships.

Some work is also being carried out on growth in alkaline gels and some clear hexagonal platelets (2 mm diameter) have been produced which are believed to be the first crystals of  $\text{Pb}(\text{OH})_2$  ever obtained. Crystal form and lattice parameters agree with predictions based on crystal-chemical arguments.

It has been gratifying to learn that several other laboratories have now taken up research in this field. The method has obvious potentialities for the production of crystals which (as far as can be ascertained) cannot be produced in other ways. Beyond that, it could prove valuable specifically as a low-temperature growth method.

#### 4.2.2.

#### Plasma Synthesis \* (F. J. Vastola)

This aspect of the project has been inactive since the last report period due to the sudden departure of the graduate student. The project will be reactivated in September. In the interim the equipment has been moved to a new laboratory and is now being reassembled.

## 5. RESEARCH RESULTS: MATERIALS CHARACTERIZATION

### 5.1 Application of electron microprobe to the characterization of solids\* (E. W. White)

#### 5.1.1 General

The electron microprobe is routinely used for the chemical characterization of the materials prepared in this laboratory to the extent that results are included in papers and reports without special discussion of the instrumentation. Microprobe analyses are about as commonplace as X-ray diffractometer scans and emission spectrographic analyses.

The microprobe was moved to a more central location in the Materials Research Laboratory last December. In its new location it will become one of the basic instruments in what will soon be a complete X-ray spectroscopy laboratory. A vacuum X-ray fluorescence spectrograph will be added shortly and a high precision curved crystal X-ray spectrometer is under development. An electron diffraction instrument has been installed for use for reflection diffraction and for special electron-excitation experiments.

Continued high performance of the electron microprobe can be assured only by continued development and updating. The main spectrometer portion of the instrument was rebuilt during the past year. Crystal changers and solid state preamplifiers were installed. A light element spectrometer was added, thus making possible the analysis of all elements boron and heavier. A third scaler was added to the readout system which now permits simultaneous digital output for the three spectrometers.

#### 5.1.2 X-ray wavelength compilation

As reported earlier, it was found that available X-ray wavelength compilations were not suitable for routine microprobe research. New tables were prepared to overcome this deficiency.

The second edition of the table "X-ray Wavelength and Crystal Interchange Settings for Wavelength Geared Curved Crystal Spectrometers" was published in October 1965. It is available as Mineral Industries Experiment Station Special Publication No. 3-64. This has become a standard reference for laboratories having wavelength geared spectrometer of the type used in most microprobes. A second compilation "X-ray Emission Line Wavelength and Two-Theta Tables" has been published as ASTM Data Series DS-37 and is widely adopted by laboratories using the common Bragg X-ray spectrometers.

#### 5.1.3 X-ray spectral shifts in compounds of Si, Al, and Mg

The most interesting research use of the probe during the past year has been the continued investigation of X-ray spectral shifts. Extensive studies have been made of the silicon, aluminum and magnesium K-emission bands. Simple oxide and silicate compounds were chosen for these studies because a large number of well characterized materials are available for which the precise crystal structure parameters have been determined. In the case of silicon which is tetravalent and tetrahedrally coordinated in the silicates used in this study, a strong correlation is observed between the  $\text{SiK}_\beta$  peak shift  $\Delta$  (measured with respect to the peak position from low-quartz) and the mean Si-O bond distance as shown in Figure 1. For unknown silicate compounds, it appears that the  $\text{SiK}_\beta$  shift can be used to predict the mean Si-O bond distance with a precision equal to the best 3-D single crystal X-ray structure analysis. This is of particular significance for materials that are amorphous or finely crystalline powders, since in such cases it is impossible to do precise structure determinations. Furthermore,

there is a relation between mean Si-O bond length and silicate structure type so that one can use this new technique to predict the type of  $\text{SiO}_4$  linkage. Analogous results have been found for trivalent aluminum in aluminum silicate and aluminum oxide compounds. Figure II summarizes the shift data for all the compounds studied to date. The situation for  $\text{Al}^{3+}$  is somewhat more complicated than for  $\text{Si}^{4+}$  since aluminum is commonly found to occur in four- or six-fold coordination by oxygen. Aluminum also occasionally occurs coordinated by five oxygens. Mixed coordinations occur in some materials. Figure III illustrates the correlation between  $\text{AlK}_{\beta}$  shift (measured with respect to the peak from corundum) and mean Al-O distance where known for structures having  $\text{Al}^{3+}$  in six-fold coordination by oxygen. Tourmaline is the one exception, since  $\text{Al}^{3+}$  is coordinated by some  $\text{F}^-$  and the magnitude of the shift does depend on the coordinating anion.

These findings are being used to predict structural sites of cations in poorly characterized materials. For example, we find that  $\text{Al}^{3+}$  goes into the octahedral sites in  $\text{MgO}$  when the  $\text{Al}_2\text{O}_3$  content is on the order of 1.5 mole %. This technique will be especially useful in characterizing the structural role of elements when present in minor concentration. Work is continuing to extend this technique to a larger number of elements.

Results of these studies were presented at the First National Conference on Electron Probe Microanalysis, College Park, Maryland 4-6 May, 1966. A paper is in press on the  $\text{SiK}_{\beta}$  shift studies.

## 5.2 Characterization of gel-grown crystals

### 5.2.1 PbI<sub>2</sub> crystals

Because the growth parameters can be easily varied, the gel method lends itself well to experiments on crystal characterization as a function of growth procedure. During the last report period, work of this kind has been done under three headings, all concerned with gel-grown PbI<sub>2</sub>.

#### 5.2.1.1 Properties of semiconducting PbI<sub>2</sub>\*

(H. K. Henisch and C. Srinivasagopalan)

Taking advantage of the availability of excellent PbI<sub>2</sub> crystals, some measurements have been made of the electric and thermoelectric properties. In particular, recombination lifetimes have been determined. A short paper on this subject has been accepted for publication in Solid State Communications and will shortly appear. (This sub-project, though closely related to the present work, was not ARPA supported).

#### 5.2.1.2 Optical and photo-electric properties of gel-grown

#### PbI<sub>2</sub> crystals \*

(H. K. Henisch and A. Dugan)

The work under this heading was carried out partly for characterizing purposes and partly in order to resolve a number of controversies and discrepancies in the literature. Preliminary results are available and can be summarized as follows.

When lead iodide crystals are grown at low temperatures ( $\sim 10^{\circ}\text{C}$ ) some crystals have dimensions parallel to the c-axis of several millimeters. Crystals of this type have been used in room temperature optical absorption measurements with light passing the a-direction. It has been found that light polarized  $\perp$  c-axis has an absorption edge at  $\sim 2.249\text{eV}$  while

light polarized parallel to c-axis has an absorption edge at  $\sim 2.285\text{eV}$ . These values taken for an absorption coefficient of  $\sim 100\text{ cm}^{-1}$ .

The temperature dependence of the absorption edge of  $\text{PbI}_2$  for light passing along the c-axis as well as the photoresponse spectrum have been measured. Measurements to date indicate that the value of  $(\Delta E/\Delta T)_p$  is dependent upon the absorption coefficient. A typical value of  $\Delta E/\Delta T$  is  $\sim 8.0 \times 10^{-9}\text{ eV}/^\circ\text{K}$  over temperature range  $150-430^\circ\text{K}$  for a value of the absorption coefficient  $\sim 100\text{cm}^{-1}$ . The only other value reported for  $(\Delta E/\Delta T)_p$  is  $5.0 \times 10^{-4}\text{ eV}/^\circ\text{K}$  but no value of the absorption coefficient is reported along with it. The optical measurements also indicate an impurity tail in the absorption edge with an absorption coefficient of  $\sim 10\text{cm}^{-1}$ .

Electrical measurements have proceeded on  $\text{PbI}_2$  using gold contacts which have been shown to be ohmic for low voltages. A plot of dark current vs  $1/T$  yields an activation energy of  $\sim 0.25\text{eV}$ . This, coupled with thermoelectric power measurements which indicate p-type conduction, would suggest an acceptor level at  $0.25\text{eV}$  above the valence band. A detailed explanation is not yet available but it appears that this activation energy does not depend upon dopants. The resistivity parallel to the c-axis has been found to be  $\sim 10^{12}\Omega\text{-cm}$ . at  $300^\circ\text{K}$ .

Growth experiments of  $\text{PbI}_2$  with different dopants have continued and some preliminary thermally stimulated current measurements have been made. Some crystals doped with thallium have exhibited glow current peaks at  $\sim 290^\circ\text{K}$ . However, not all

crystal of  $\text{PbI}_2$  grown with Tl doping exhibit this peak. Measurements will be continued to determine under which growth conditions the peaks are more pronounced. Super-linearity of photoconductive response in both pure and Sn-doped crystals of  $\text{PbI}_2$  has been detected. The super-linearity is more pronounced in Sn-doped crystals.

#### 5.2.1.3 Polytypism in gel-grown $\text{PbI}_2$ crystals\*

(V. Vand and J. I. Hanoka)

The work referred to in the last report was continued and a paper on this subject (by J. I. Hanoka, K. Vedam and H. K. Henisch) with the above title was presented at the recent International Conference on Crystal Growth in Boston. It will be published shortly in the J. Phys. Chem. Solids.

From about January, 1966, this work has been under the supervision of Dr. V. Vand. Since this time, 2 major results have been found.

First, it has been discovered that the distribution of all the rhombohedral polytypes (6R, 12SR, 18R, etc.) found over the entire range of growth conditions follows a Poisson distribution of the form

$$P_s = \frac{e^{-m} m^s}{s!}$$

where  $P_s$  is the probability,  $s$  is a parameter which here = 12 and  $m = 6, 12, 18, 24, 30 \dots$

The second major result is that it is now possible to separate physically different polytypes which are syntactically coalesced in a direction parallel to the c-axis. The crystals

with which this can be done do not show the plate habit and instead have comparatively large dimensions in the c direction. It has been found that by using the right concentrations of reagents in the gel and also using temperatures slightly below room temperature, such crystals can be readily grown. We have shown that crystals of this habit may have different polytypes "stacked" one on top of another along the c-axis. Using a razor blade fastened to a micro-manipulator and working under a stereo microscope, such crystals have been sliced in planes l to the c-axis. In one particular case, a crystal was sliced into 19 slices, each 0.08 mm. thick, and, these slices were then x-rayed. Four different polytypes present in this crystal were then found to be physically separated. We are exploiting this result in an experiment in which we are now attempting to measure the growth rate of different polytypes.

We have found evidence supporting the view that polytypism is generated by a screw dislocation mechanism. In particular, some of our observations suggest that the screw dislocation is formed by the imperfect matching of an epitaxial layer of PbI<sub>2</sub> growing on a "dirt" particle. We are now exploring the possible use of electron microscopy and the electron-microprobe in order to elucidate this question more fully.

### 5.3 Surface studies of lithium fluoride in varying ambient atmosphere\* (S. R. Sashital and K. Vedam)

In the previous report (January 1, 1965 to June 30, 1965) observations and conclusions on the effect of ambient atmospheres on the mechanical properties of LiF and NaF were reported.

Although this report<sup>(1)</sup> contained mainly the observations on

embrittlement of alkali fluorides on aging in ambient atmospheres, yield point changes were also reported. The above mentioned effects were observed in '4-point loading' bending experiments. According to Gilman<sup>(2)</sup> the yield point changes, indirectly reflecting the hardness properties of crystals, so observed, are not completely reliable. Consequently a different type of measurement on these crystals has been resorted to for obtaining direct information on hardness changes due to aging in ambient atmospheres.

It has been previously proposed<sup>(2)</sup> that the influence of surface contamination due to atmosphere does not affect the initial motion of dislocations at low stress levels, but any effects of the contamination are observed only in the changes of the stress-strain curves after the onset of initial yielding. If, instead of the 'yield point' as a measure of the hardness, one defines hardness, in accordance with Vaughn & Davison<sup>(3)</sup>, as the ease with which dislocations can be generated and moved, some information could be gained about the small hardness changes due to atmospheric contamination. By this definition, therefore, small hardness changes will be shown in the differences of the glide lengths of dislocations propagating from an indentation produced by a standard device such as the Vicker's hardness tester. This report will show that earlier<sup>(1)</sup> measurements on ductility changes and the proposed mechanism for surface contamination are supported by the 'hardness' measurements performed as described above. High purity LiF blanks<sup>(4)</sup> were irradiated with 500,000 r of x-rays. The hardening due to irradiation facilitated good cleavage of the

crystals into rectangular beam - pairs with matching freshly cleaved surfaces. The cleaving was performed under xylene, which is fairly free of oxygen, to prevent any contamination by atmosphere. One part of each pair was preserved in xylene in the fresh condition, while its matching counterpart was aged either in oxygen, air or nitrogen as required. Microhardness indentations were made with a Vickers diamond pyramid on a Leitz microhardness tester under a load of 25 mgs. In some cases dislocation-half loops were deliberately introduced on the crystal surface by dropping 600 mesh SiC powder from a height of 8 inches.

The reagent used for etching crystal surfaces subsequent to indentation was an aqueous  $\text{FeCl}_3$  solution ( $3 \times 10^{-5} \text{M}$ ). Dislocation loop lengths originating from indentations were measured at a magnification 300x with a filar micrometer eyepiece of least count  $2.7\mu$ .

As has been reported by Vaughn & Davison<sup>(3)</sup>, when stresses are already present in the crystals prior to test, the etch pit pattern of dislocation loops is asymmetric around the indentation. In a large majority of our observations the etch pit patterns were symmetrical, probably due to the extreme care taken in the handling of the specimens. Tables I through V indicate the differences in the glide lengths of the dislocation loops due to the various aging treatments. It is seen that aging in air results in a glide length decrease of approximately 8 - 9%, while aging in nitrogen does not affect the glide lengths, or, at any rate, the differences are within the range of experimental error. The introduction of artificial sources

due to sprinkling is further seen to result in a larger decrease in many cases as compared to the unsprinkled crystals. It is also seen that polishing the crystals with a 1.5%  $\text{NH}_4\text{OH}$  aqueous solution results in an almost complete absence of glide length decrease.

As was proposed previously<sup>(1)</sup> the mechanical property changes due to atmospheric contamination seem to arise from the substitution of surface  $\text{F}^-$  ions by  $\text{O}^{--}$  ions. Such a substitution, probably arising out of ionization (of oxygen atoms) by high electric fields localized at point of dislocation emergence<sup>(5)</sup> on the surface, must, however, be accompanied by creation of  $\text{F}^-$  vacancies by the requirement of charge neutrality. The probable formation of associated  $\text{O}^{2-}$  impurity -  $\text{F}^-$  vacancy pairs will give rise to tetragonal distortions in the surface layers. The asymmetric strain fields of such tetragonal distortions have been shown<sup>(6,7)</sup> to interact rather strongly with mobile dislocations as compared to the interactions between symmetrical defects (e.g. substitutional  $(\text{OH}^-)$  ions) and dislocations.

In view of the 'adsorption locking' hypothesis by Westwood<sup>(8)</sup>, it appears that the confinement of these  $\text{O}^{2-}$  -  $\text{F}^-$  vacancy pairs to only the surface layers could still be effective in influencing the glide lengths of dislocations moving under a stress. The presence of dislocations emerging from the surface layers seems to be a necessity for the hardening process. The differences in the amount of hardening for two crystals aged under identical conditions could probably have their origin in the differences of dislocation source distribution on the surfaces.

Table I

Dislocation glide lengths in "fresh" and matching "air" aged crystals

Crystal	Dislocation glide length	% Decrease of glide length
1 U fresh	$27.93 \times 10^{-3}$ cms	9.1%
1 U aged: 8 days	$25.60 \times 10^{-3}$ cms	
3 U fresh	$25.52 \times 10^{-3}$ cms	8.6%
3 U aged: 8 days	$23.31 \times 10^{-3}$ cms	

Table II

Glide lengths in crystals sprinkled with SiC 600 mesh powder and aged for 8 days in air

Crystal	Dislocation glide length	% Decrease in glide length
2 S fresh	$29.8 \times 10^{-3}$ cms	35%
2 S aged: 8 days	$18.93 \times 10^{-3}$ cms	
3 S fresh	$30.3 \times 10^{-3}$ cms	21%
3 S aged: 8 days	$23.86 \times 10^{-3}$ cms	

Table III

Glide lengths in crystals polished for 15 minutes ( $\text{NH}_4\text{OH}$  1.5%); aged for 8 days

Crystal	Dislocation glide length	% Decrease of glide length
b polished, fresh	$13.11 \times 10^{-3}$ cms	0.07%
b* polished, aged	$13.10 \times 10^{-3}$ cms	
c polished, fresh	$13.11 \times 10^{-3}$ cms	0.4%
c* polished, aged	$13.05 \times 10^{-3}$ cms	

Table IV

Crystals aged in dry nitrogen for 5 days

<u>Crystal</u>	<u>Dislocation glide length</u>	<u>% Decrease in glide length</u>
1x - fresh	$20.41 \times 10^{-3}$ cms	2%
1*x - nitrogen	$19.94 \times 10^{-3}$ cms	
2x - fresh	$21.05 \times 10^{-3}$ cms	-2.3%
2*x - nitrogen	$22.55 \times 10^{-3}$ cms	
3x - fresh	$19.51 \times 10^{-3}$ cms	0.5%
3*x - nitrogen	$20.60 \times 10^{-3}$ cms	

Table V

Crystals aged in dry oxygen for 4 days

<u>Crystal</u>	<u>Dislocation glide length</u>	<u>% Decrease in glide length</u>
1c - fresh	$23.56 \times 10^{-3}$ cms	10%
1*c - oxygen	$21.06 \times 10^{-3}$ cms	
2c - fresh	$17.57 \times 10^{-3}$ cms	$\approx 4\%$
2*c - oxygen	$16.93 \times 10^{-3}$ cms	

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#### 5.4 Dislocation studies by X-ray methods\* (H. A. McKinstry and D. R. Lundy)

X-ray topographical methods as exemplified by the Berg-Barrett technique<sup>(1)</sup> and the parallel beam method<sup>(2)</sup> developed by Barth have been used to study the alteration in crystal perfection as induced by mechanical treatment. The technique used is that described by Newkirk<sup>(1)</sup> to determine the orientation of the Burger's vector by using topographic photographs of the same surface in the light 'reflected' from different planes.

In the freshly cleaved sample, the preponderance of lines are diagonal. This would correspond to edge type dislocations. The exact direction of the Burger's vector could not be determined since changing the plane of reflection did not introduce a marked change in the intensity. This is the necessary requirement for determining Burger's vector orientation.

The worked sample images, by comparison, are much less distinct than the freshly cleaved ones. This is in all probability due to the increase in the number of dislocations generated during plastic working of the sample. As the dislocations increase, the resolution of individual lines decreases and the image loses cleanliness.

Examination of the cleavage face of Ge confirmed the hypothesis that the dislocations occur at cleavage steps on the surface. This was an aid to another graduate student, W. Noble, who made this postulation in connection with his measurements on the surface conductivity of Ge.

#### References

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5.5 Studies of crystal perfection by density and X-ray techniques \*  
(H. A. McKinstry and W. Stitt)

5.5.1 Hot-pressed MgF<sub>2</sub>

A sample of hot pressed MgF<sub>2</sub> transparent, and presumably, theoretically dense, furnished by the Bausch and Lomb Company, was examined for its perfection since certain anomalous density values (< 100% theoretical) had been reported on such material. It was anticipated that the material would be in a strained state. However, by comparison of the X-ray diffraction peak width with peaks from unstrained material of comparable absorption coefficients it is obvious that very little microstrain exists in the sample. It is interesting to note that it was not possible for us to obtain MgF<sub>2</sub> from any other source which showed as little peak broadening as this hot pressed sample did.

The density, obtained by the hydrostatic weighing of an 8 gm sample, was 3.1718 with an estimated standard deviation of 0.0003 based on three measurements. This is a lower density than has been reported for comparable material<sup>(1)</sup>.

The lattice parameters for this tetragonal material were refined by a newly written computer program using a weighting factor for each peak measured. The lattice parameters as measured for this hot pressed material differ significantly from literature values as indicated in Table 1.

Table 1

Lattice Parameters for MgF<sub>2</sub> and Theoretical Density

	Hot Pressed MRL (1966)	Powdered Rao et al <sup>(2)</sup> (1962)	Powdered Swanson et al <sup>(3)</sup> (1953)	Measured Density <sup>(4)</sup>
"a" dimension a(Å)	4.6188	4.6216	4.623	
"c" dimension c(Å)	3.0527	3.0532	3.052	
density (gm/cm <sup>3</sup> )	3.1772	3.1729	3.172	3.1766

It is interesting to note that there is a greater difference in the "a" value (0.0028Å) than in the "c" value (0.0005Å).

On the basis of the values measured here the material is 99.8% of its theoretical density, although it is easy to see how a measured value somewhat above the 3.172 value of Swanson et al could be obtained.

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### 5.5.2 Precision of lattice parameters of silicon

These studies are aimed at absolute point defect characterization by maximum-precision lattice parameter and density measurements. The results of the International Union of Crystallography precision lattice parameter project<sup>(1)</sup> showed that the agreement among laboratories for the lattice parameter of silicon is much lower ( $\sim 1$  part in  $10^4$ ) than the precision claimed by most laboratories (usually 1 part in  $10^5$ ). The average of twenty-five values used in this international project gave  $a = 5.43054^\circ\text{A}$  with a standard deviation of  $.00017^\circ\text{A}$ ; however, only two of the sixteen reporting laboratories used diffractometers.

Smakula<sup>(2)</sup> using a diffractometer found  $a = 5.43072^\circ\text{A}$  with an estimated error of  $0.00002^\circ\text{A}$ , by measuring 100 ohm-cm. silicon which had been crushed into powder.

A sample of silicon with the same resistivity was measured here. In an attempt to remove the systematic errors involved in the measurements by the diffractometer, the lattice parameter as calculated from all diffraction peaks above  $100^\circ 2\theta$  were weighted by the factor of  $\tan^2\theta$  and extrapolated by least squares vs.  $\cos^2\theta / \sin\theta$ . Using the two theta values given by Smakula this method gave  $a = 5.43074^\circ\text{A}$  with an estimated standard deviation of better than  $0.00001$ . This compares very favorably with Smakula's result, confirming that this technique is similar and not the cause for the difference noted below.

Two sets of measurements using only those peaks for which diffraction angle was greater than  $100^\circ 2\theta$  gave values  $a = 5.43060$  and  $5.43062$  with the statistical estimate of the standard deviation less than  $\sigma = .00002$  for both measurements.

This lack of precision indicates that source of the systematic error, though small, is still not known. High precision values reported in the literature are cited for purposes of convenient comparison.

Bond, single crystal 5.43073 (3)

Bearden, single crystal 5.43070 (4)

Straumanis, single crystal 5.43048; powder, 5.43081 (5)

It becomes clear that absolute lattice parameter measurements cannot as of 1966 be trusted beyond 1 part in 50,000, although relative measurements appear to be reproducible under our condition to 1 part in 500,000. Studies on the changes of lattice parameter and density on "grinding" are now being finalized.

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5.6 Use of a laser ultramicroscope for detection of imperfections in crystals \*

(V. Vand and K. Vedam)

This work has produced very useful and interesting results showing that light scattering is a NEW and easily used routine tool capable of detecting imperfections more easily than by any other means, and probably some not detectable by any other means. A very recent paper, "Use of Laser as a Source of Light for Ultramicroscopy and Light Scattering by Imperfections in Crystals. Investigation of Imperfections in LiF, MgO and Ruby", J. Appl. Phys., July 1966, summarizes our findings.

Our own work is being developed towards the use of a 100 watt laser, while other Federal agencies have already contracted for building such instruments for inspecting crystals.

6. FUTURE PLANS

Most of the lines of work which are currently active will be continued. Some changes will be made along the following lines:

6.1 Personnel:

Dr. R. E. Newnham, Associate Professor of Electrical Engineering at M.I.T. will be joining our faculty in August. Professor Newnham has been a senior member of the materials preparation and crystal structure analysis team in the group under Professor von Hippel. He will continue his optical, magnetic and x-ray methods of structure analysis of new materials, and will have a major responsibility within this contract.

6.2 Research areas

The flux growth work as such is now being curtailed somewhat and directed into a more detailed and sophisticated analysis of

the structure of the flux or "solution", and into the study of nucleation processes. The hydrothermal work is being channeled in two directions: the growth of larger, doped, more perfect crystals for measurements on the one hand, and growth under the more complex condition of S-L-V equilibrium on the other. Greater emphasis will also be placed on exploiting the successful beginnings in vapor pyrolysis work.

The x-ray emission studies will move toward greater refinement to extend the sensitivity of the method, which is now its limiting feature as a general characterization tool. As far as surface characterization is concerned, the mechanical-property study will probably be completed, and the general potential of the laser-microprobe mass spectrometer will be evaluated. It is intended to extend the work on crystal growth in gels towards higher temperature and pressure conditions and, as far as possible, to place special emphasis on the growth of crystals with potential electronic applications. Experiments on thermoluminescent characterization procedures are also planned, in an attempt to make assessments of trap density.

### 6.3 Communications

Penn State will be host to an International Conference on Materials Characterization November 16-18, 1966. The aim in sponsoring such an event is to emphasize the virtually indispensable role of characterization procedures in any solid state research.

A new journal, the "Materials Research Bulletin"\*, is being

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\*Pergamon Press

published and is designed specifically to emphasize crystal growth and the preparation and characterization of materials. It incorporates some novel ideas in publishing technique. Professors Henisch and Roy are Joint Editors-in-Chief, and will enjoy the cooperation of 25 Associate Editors from the United States, Canada, Great Britain, France, Germany, Japan, the Soviet Union, Holland, Belgium and Sweden. The first issue is due to appear in September.